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**WO 01/23475 A1**

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(54) Title: POLYESTER COMPOSITIONS OF LOW RESIDUAL ALDEHYDE CONTENT

(57) Abstract: A mixture of a polyester, such as poly(ethylene terephthalate) PET, and a second polymer which is polyacrylamide, polymethacrylamide or copolymer of acrylamide or methacrylamide when extrusion compounded exhibits a lower residual acetaldehyde content than does PET alone when similarly treated. The invention pertains to any polyester used in the manufacture of bottles or containers which in turn are used to store consumer materials, especially food, beverages and most especially water.

Polyester Compositions of Low Residual Aldehyde Content

A mixture of a polyester, such as poly(ethylene terephthalate) PET, and a second polymer which is polyacrylamide, polymethacrylamide or copolymer of acrylamide or methacrylamide when extrusion compounded exhibits a lower residual acetaldehyde content than does PET alone when similarly treated. The invention pertains to any polyester used in the manufacture of bottles or containers which in turn are used to store consumer materials, especially food, beverages and most especially water.

U.S. Patent 4,361,681 teaches that polyester containing anhydride end-cap agents have a reduced acetaldehyde generation rate.

U.S. Patent 5,459,224 discloses polyesters having 4-oxybenzylidene end-cap agents to impart improved weatherability and photostability, but no mention is made as to evolution of acetaldehyde. However, it is indicated that such polyesters are suitable for food and beverage packaging.

Polyesters can be synthesized by a number of routes known in the art using a variety of catalyst systems. EP-A-0 826 713 teaches that lower levels of acetaldehyde occur during copolymerization of PET when a phosphite such as bis(2,4-di-tert-butylphenyl)pentaerythritol phosphite is present during the polymerization.

U.S. Patents 4,837,115; 5,258,233; 5,266,413; 5,340,884; 5,648,032 and 5,650,469; and WO-A-93/20147; WO-A-93/23474; WO-A-98/07786 and WO-A-98/39388 teach the use of polyamides as a means of reducing the concentration of acetaldehyde, presumably via a Schiff-base reaction with the aldehyde, which is reversible in the presence of water.

U.S. Patent 5,856,385 teaches the use of polyamide or amide-wax to reduce the level of acetaldehyde which occurs when sorbitol-based clarifying agent is heated in polyolefins.

U.S. Patent 5,011,890 describes the suppression of formaldehyde formation when polyacrylamide, polymethacrylamide or selected acrylamide or methacrylamide copolymers are used in polyacetals. A requirement is that the polyacrylamide or polymethacrylamide must be "non-meltable" at the processing temperature of polyacetal. There is no suggestion in this

patent that using polyacrylamide or polymethacrylamide in a polyester would reduce the concentration of acetaldehyde in a melt-mixed blend such as via extrusion.

The invention is useful for any polyester where aldehydic compounds, especially acetaldehyde, are formed or evolved during thermal processing of said polyester. Thermal processing of PET includes the synthesis of PET, thermal exposure during solid state polymerization (SSP), any injection molding, injection-blow molding or stretch-blow molding used in the manufacture of preforms, parissons or bottles and containers, or extrusion of film, or during any melt processing of PET above its glass transition temperature and below its decomposition temperature.

The instant invention provides for a lower amount of contaminants (e.g. aldehydes) in PET water bottles thus providing for improved taste or flavor in bottled water or other bottled beverages in said PET containers. The reduction in the amount of acetaldehyde is highly beneficial in this respect. Acetaldehyde is known as a decomposition product of polyesters such as PET. The acetaldehyde imparts an undesirable taste or flavor to bottled water stored in PET bottles. It has been a long sought objective of the industry to reduce the level of acetaldehyde which migrates out of the PET bottle walls into the water or other beverage stored therein. A number of engineering or design changes to extruders, injection molding machines for preforms and bottle making machinery have been made to minimize formation of acetaldehyde when poly(ethylene terephthalate) PET is processed. Modification to the PET composition itself have been made to lower its melting point or its melt viscosity in order to allow less severe thermal or mechanical damage when PET is processed into preforms or bottles.

The instant invention pertains to a polyester composition, stabilized against the formation of aldehydic contaminants during melt processing of said polyester, which comprises

- (a) a polyester, and
- (b) an effective stabilizing amount of a second polymer which is a polyacrylamide, polymethacrylamide or an acrylamide or methacrylamide copolymer with at least one ethylenically unsubstituted comonomer.

- 3 -

The polyester of component (a) is 95-99.9 % by weight of the stabilized composition; and the second polymer of component (b) is 5 to 0.1 % by weight, preferably 1 to 0.1 % by weight, of the stabilized composition.

The polyester of component (a) has dicarboxylic acid repeat units selected from the group consisting of aromatic dicarboxylic acids having 8 to 14 carbon atoms, aliphatic dicarboxylic acids having 4 to 12 carbon atoms, cycloaliphatic dicarboxylic acids having 8 to 12 carbon atoms, and mixtures thereof.

Preferably such diacids are terephthalic acid, isophthalic acid, o-phthalic acid, naphthalene dicarboxylic acid, cyclohexane dicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, sebacic acid and mixtures thereof.

Especially preferred are terephthalic acid and 2,6-naphthalene dicarboxylic acid.

The diol or glycol portion of the polyester of component (a) are derived from the generic formula HO-R-OH where R is an aliphatic, cycloaliphatic or aromatic moiety of 2 to 18 carbon atoms.

Preferably such diols or glycols are ethylene glycol, diethylene glycol, triethylene glycol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 1,4-cyclohexanedi-methanol, 3-methylpentane-2,4-diol, 2-methylpentane-1,4-diol, 2,2-diethylpropane-1,3-diol, 1,4-di-(hydroxyethoxy)benzene, 2,2-bis(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethylcyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)propane, 2,2-bis-(4-hydroxypropoxyphenyl)ethane and mixtures thereof.

Most preferably, the diol is ethylene glycol.

The polyester of component (a) is preferably poly(ethylene terephthalate) PET or poly(ethylene 2,6-naphthalene-2,6-dicarboxylate); most preferably poly(ethylene terephthalate).

It is also contemplated that the polyester of component (a) can also be a blend of polyesters or copolyesters including components mentioned above.

- 4 -

It is contemplated that the polyester of component (a) can be virgin polymer or alternatively polymer recyclate. Additionally, it is possible to combine 80-99 % by weight of a polyester with 20-1 % by weight of a concentrate where the concentrate comprises 10-90 % by weight of a polyester carrier resin and 90-10 % by weight of a second polymer described for component (b).

The second polymer of component (b) is any polymer which contains a polymerized acrylamide or methacrylamide repeating unit. The preparation of acrylamide or methacrylamide polymers is generally known.

Preferably, the second polymer is polyacrylamide, polymethacrylamide or a copolymer of acrylamide or methacrylamide with another ethylenically unsaturated monomer such as acrylamide, methacrylamide, styrene, ethylene, an alkyl acrylate, an alkyl methacrylate, 2-dimethylaminoethyl methacrylate, N-vinyl-2-pyrrolidinone or acrylonitrile.

Most preferably, the second polymer of component (b) is polyacrylamide [PERCOL 333 (RTM), Ciba] or polyacrylamide [PERCOL 351 (RTM), Ciba].

The copolymers of component (b) can be random or block copolymers.

It is also contemplated that the compositions may contain other components or modifiers such as stabilizers, dispersants, pigments, colorants, UV absorbers, antioxidants, toughening agents, nucleating agents and fillers as described in U.S. Patent 5,011,890, the pertinent parts of which are incorporated herein by reference.

The instant invention also pertains to a process for preventing the formation of aldehydic contaminants during melt process of a polyester which comprises incorporating into said polyester an effective stabilizing amount of a second polymer which is polyacrylamide, polymethacrylamide or an acrylamide or methacrylamide copolymer with at least one ethylenically unsubstituted comonomer.

A preferred embodiment of the present invention is the use of component (b) as a stabilizer for preventing the formation of aldehydic contaminants during melt processing of a polyester.

The instant invention also pertains to a process for forming a bottle preform or a PET bottle or container suitable for storing water (mineral, natural, ozonated) or other foodstuffs, which allows the desirable taste of the water or foodstuff after packaging to remain unaltered after being placed in said bottle or container prepared from the polyester composition of the instant invention.

The following examples are for illustrative purposes only and are not to be construed to limit the scope of the instant invention in any manner whatsoever.

General: PET bottle grade pellets are subjected to extrusion compounding to simulate the heat history which PET experiences when thermally injection molded into bottle preforms and subsequently stretch-blow molded into bottles. The efficacy of an additive added to reduce the formation of acetaldehyde is determined by quantitative analysis using thermal desorption GC-MS after adaption of published methods. An unstabilized PET is extruded each day to provide a control polymer for measuring acetaldehyde formation.

Extrusion: PET is predried in vacuo under nitrogen at an oven temperature of about 70°C to a moisture level of about 30 ppm which is verified on a Mitsubishi VA-O6 moisturemeter. A Leistritz 18 mm or 27 mm corotating, non-intermeshing twin screw extruder is configured as follows: set temps = throat (220-230°C), zones and die (270°C), actual extrudate melt temperature is 275-280°C, screw at 100-110 rpm, hopper feeder = 10-15 ppm.

PET Pellet Color: Yellowness Index (YI), and L\*, a\*, b\* by ASTM D1925, D65 10degm specular included, measured on PET pellets using a DCI spectrophotometer.

Acetaldehyde Analysis: The concentration of acetaldehyde in PET is quantitatively determined using a thermal desorption GC-MS method adapted from B. Nijassen et al., Packaging Technology and Science, 9, 175 (1996); S. Yong Lee, SPE ANTEC 1997, pp 857-861; and M. Dong et al., J. Chromatographic Science, 18, 242 (1980). A general example follows below:

The PET samples are analyzed, in duplicate, by weighing 250 mg of powdered PET pellets (cryogenically pulverized) in a 5 ml crimp sealed headspace vial. The sample vial is heated at 120°C for one hour in a Tekmar model 5000 static headspace analyzer. The headspace

gas (5 cc) is then transferred via a heated transfer line to a Fisons MD-800 GC-MS system for SIR detection of the acetaldehyde. The acetaldehyde is detected by monitoring its fragment ions of 29 and 44 m/e. The Total Ion Current (TIC) of the GC-MS is also monitored in the retention time region of 4-8 minutes. By doing this the presence of acetaldehyde in the samples is confirmed by three different detectors. By using a known acetaldehyde value for PET, the ration of peak areas for the known PET resin and for the experimental PET resin blends are compared and the amount of acetaldehyde in the experimental blend can be obtained.

Example 1: Stabilization of PET.

Unstabilized commercial PET [Cleartuf 7207 (RTM), Shell] is used as a control PET. The additive listed below demonstrates a significant reduction in the amount of acetaldehyde (AA) versus the amount seen when unstabilized PET is extrusion compounded. The total ion current (TIC) data run in triplicate for the control PET has a standard deviation of  $\sigma = 0.35$ . The results are summarized in Table 1.

Table 1:

Example	Additive weight %	% AA Reduction	TIC ave ppm AA
1a <sup>a)</sup>	—	—	2.4
1b <sup>b)</sup>	0.25 % A <sup>c)</sup>	12	2.1

a) Example for comparison.

b) Example according to the invention.

c) A is polyacrylamide [PERCOL 333 (RTM), Ciba].

The use of the polyacrylamide results in the reduction of acetaldehyde versus the control.

Example 2: Stabilization of PET.

Unstabilized commercial PET [Cleartuf 7207 (RTM), Shell] is used as a control PET. The additive listed below demonstrates a significant reduction in the amount of acetaldehyde

(AA) versus the amount seen when unstabilized PET is extrusion compounded. The total ion current (TIC) data run in triplicate for the control PET as a standard deviation of  $\sigma = 0.35$ . The results are summarized in Table 2.

Table 2:

Example	Additive weight %	% AA Reduction	TIC ave ppm AA
2a <sup>a)</sup>	—	—	2.1
2b <sup>b)</sup>	0.25 % B <sup>d)</sup>	19	1.7

a) Example for comparison.

b) Example according to the invention.

d) B is polyacrylamide [PERCOL 351 (RTM), Ciba].

The use of the polyacrylamide results in the reduction of acetaldehyde versus the control.

Example 3: Stabilization of PET.

When following the general procedure described in Example 1, the addition of the polyacrylamides as prepared in U.S. Patent 5,011,890 to the PET before extrusion compounding results in reduced levels of acetaldehyde formation during extrusion compounding:



What is claimed is:

1. A polyester composition, stabilized against the formation of aldehydic contaminants during melt processing of said polyester, which comprises
  - (a) a polyester, and
  - (b) an effective stabilizing amount of a second polymer which is polyacrylamide, polymethacrylamide or an acrylamide or methacrylamide copolymer with at least one ethylenically unsubstituted comonomer.
2. A composition according to claim 1 wherein the polyester of component (a) is 95-99.9 % by weight of the stabilized composition; and the second polymer of component (b) is 5 to 0.1 % by weight of the stabilized composition.
3. A composition according to claim 1 wherein the polyester of component (a) has dicarboxylic acid repeat units selected from the group consisting of aromatic dicarboxylic acids having 8 to 14 carbon atoms, aliphatic dicarboxylic acids having 4 to 12 carbon atoms, cycloaliphatic dicarboxylic acids having 8 to 12 carbon atoms, and mixtures thereof.
4. A composition according to claim 3 wherein the dicarboxylic acid is terephthalic acid, isophthalic acid, o-phthalic acid, naphthalene dicarboxylic acid, cyclohexane dicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, sebacic acid and mixtures thereof.
5. A composition according to claim 4 wherein the dicarboxylic acid is terephthalic acid or 2,6-naphthalene dicarboxylic acid.
6. A composition according to claim 1 wherein the diol portion of the polyester of component (a) is derived from the generic formula HO-R-OH where R is an aliphatic, cycloaliphatic or aromatic moiety of 2 to 18 carbon atoms.
7. A composition according to claim 6 wherein the diol is ethylene glycol, diethylene glycol, triethylene glycol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 1,4-cyclohexanedimethanol, 3-methylpentane-2,4-diol, 2-methylpentane-1,4-diol, 2,2-diethylpropane-1,3-diol, 1,4-di-(hydroxyethoxy)benzene, 2,2-bis(4-hydroxycyclohexyl)-propane, 2,4-

dihydroxy-1,1,3,3-tetramethylcyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)propane, 2,2-bis-(4-hydroxypropoxyphenyl)ethane and mixtures thereof.

8. A composition according to claim 7 wherein the diol is ethylene glycol.

9. A composition according to claim 1 wherein the polyester of component (a) is poly(ethylene terephthalate) or poly(ethylene 2,6-naphthalene-2,6-dicarboxylate).

10. A composition according to claim 9 wherein the polyester is poly(ethylene terephthalate).

11. A composition according to claim 1 wherein the second polymer of component (b) is any polymer which contains a polymerized acrylamide or methacrylamide repeating unit.

12. A composition according to claim 11 wherein the second polymer of component (b) is polyacrylamide, polymethacrylamide or a copolymer of acrylamide or methacrylamide with another ethylenically unsaturated monomer which is acrylamide, methacrylamide, styrene, ethylene, an alkyl acrylate, an alkyl methacrylate, 2-dimethylaminoethyl methacrylate, N-vinyl-2-pyrrolidinone or acrylonitrile.

13. A composition according to claim 11 wherein the second polymer of component (b) is polyacrylamide.

14. A process for preventing the formation of aldehydic contaminants during melt process of a polyester which comprises incorporating into said polyester an effective stabilizing amount of a second polymer which is polyacrylamide, polymethacrylamide or an acrylamide or methacrylamide copolymer with at least one ethylenically unsubstituted comonomer.

15. Use of a polyacrylamide, polymethacrylamide or an acrylamide or methacrylamide copolymer with at least one ethylenically unsubstituted comonomer as stabilizer for preventing the formation of aldehydic contaminants during melt processing of a polyester.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/09198

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L67/02 //(C08L67/02,33:24)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2 848 432 A (SCHULKEN ET AL.) 19 August 1958 (1958-08-19) claims 1-6.	1-13
X	US 2 996 475 A (JOYNER ET AL.) 15 August 1961 (1961-08-15) claims 1-13	1-13
X	FR 2 372 199 A (CIBA GEIGY AG) 23 June 1978 (1978-06-23) page 9, line 34 -page 10, line 21; claims 1-5,14; example 8	1-13



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 2848432	A	19-08-1958	NONE	
US 2996475	A	15-08-1961	NONE	
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			DE 2751969 A	01-06-1978
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			NL 7712855 A	26-05-1978